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(54) **Styrene-based polymer compositions**

Polymermischungen auf Styrolbasis

Compositions polymérique à base de styrène

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Description

1. Field of the Invention

This invention relates to a styrene-based polymer composition. More specifically, it relates to a styrene-based polymer composition which is suitable for materials such as the exterior trim parts of an automobile, engine compartment parts, machine parts, electric and electronic parts, domestic kitchenware, etc. a stretched molding thereof and a process for efficiently producing the stretched molding.

2. Description of the Related Arts

Heretofore, a composition which comprises a polyphenylene ether resin (polyphenylene oxide) (hereinafter referred to as "PPE") and a styrene-based polymer has been widely used as engineering plastics which are excellent in mechanical properties and heat resistance. Such compositions have been described in, for example, Japanese Patent Applications Laid-Open No. 5085/1971 and No. 39457/1972, and U.S. Patent No. 3,383,435.

However, these compositions have serious drawbacks in that solvent resistance, particularly resistance to aromatic hydrocarbon type solvents, is little, whereby their uses are limited. This can be considered as an essential drawback belonging to the styrene-based polymer having atactic configuration as one component of the composition.

Also, PPE generally has self-extinguishing properties and therefore, a resin composition containing PPE also has flame retardance to some degree. However, demands on flame retardance in electric and electronic fields and automobile fields in recent years has become increasingly severe, so that the above demands cannot be satisfied with the flame retardance due to the self-extinguishing properties which PPE originally has.

In general, styrene-based polymers have been prepared by radical polymerization. The styrene-based polymers thus prepared have atactic configuration in streoregularity. However, in such styrene-based polymers, improvement in physical properties by stretching cannot be expected. Also, styrene-based polymers having isotactic configuration in stereoregularity have also been known and an attempt to stretch the polymer has been made (Polymer Chemistry, vol., 21, p. 206 (1964)). However, the styrene-based polymers have slow crystallization rate and its crystalline structure is helical so that sufficient stretching effect cannot be essentially obtained.

The group of the present inventors' has proposed a process for producing a film-like molding by stretching a styrene-based polymer having mainly syndiotactic configuration and a resin composition comprising the above styrene-based polymer and other thermoplastic resins and/or rubber in Japanese Patent Applications No. 3847/1988, No. 4921/1988, No. 4923/1988 and No. 4924/1988. In these applications, a low molecular weight PPE having a molecular weight of 10,000 or less is disclosed as one example of the thermoplastic resin.

However, after further investigation concerning the composition, it has found that there is room for further improvement since mechanical properties, solvent resistance and flame retardance are insufficient due to low molecular weight of PPE.

Also, as proposed in the above Japanese Patent Application No. 3847/1988, the above styrene-based polymer becomes a stretched molding having excellent transparency and high modulus of elasticity by stretching. However, this stretched molding has a disadvantage in that its mechanical strength is low, as compared with stretched polyester film or polyamide film. Therefore, in order to improve its mechanical strength, an attempt of blending the aforesaid styrene-based polymer having syndiotactic configuration with other resins (particularly a low molecular weight PPE) has been made (Japanese Patent Application No. 4921/1988).

However, according to research thereafter, it has been found that this blended material is still insufficient in mechanical strength of its stretched molding due to the low molecular weight of PPE.

EP-A-0 314 146 discloses thermoplastic compositions based on syndiotactic polymers of styrene and polyphenylene ethers.

EP-A-0 291 915 refers to syndiotactic styrene-based resin compositions and mouldings produced from said compositions.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a styrene-based polymer composition which can produce a molding improved in mechanical properties and solvent resistance.

Also, another object of the present invention is to provide a styrene-based polymer composition which is excellent in the above mechanical properties and solvent resistance as well as flame retardance.

The present invention is to provide a styrene-based polymer composition which comprises

(A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of

30% or more and
(B) 90 to 2% by weight of PPE having an intrinsic viscosity of 0.28 dl/g or more at 30°C in chloroform, and
(C) 3 to 40 parts by weight of a flame retarder and
(D) 1 to 15 parts by weight of a flame-retardant aid based on 100 parts by weight of the total amount of (A) and (B).

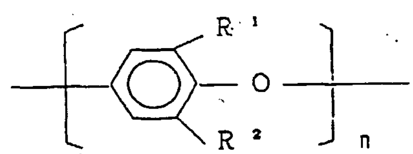
DESCRIPTION OF PREFERRED EMBODIMENTS

The styrene-based polymer composition of the present invention comprises the above components (A) and (B) as main components. Here, the component (A) is a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more, and the syndiotactic configuration means that a stereostructure is mainly syndiotactic, i.e., the stereostructure in which phenyl groups or substituted phenyl groups as side chains are located alternately at opposite directions relative to the main chain consisting of carbon-carbon bonds. The tacticity is quantitatively determined by the nuclear magnetic resonance method using carbon isotope (^{13}C-NMR) method. The tacticity as determined by the ^{13}C-NMR method can be indicated in terms of proportions of structural units continuously connected to each other, i.e., a diad in which two structural units are connected to each other, a triad in which three structural units are connected to each other, or pentad in which five structural units are connected to each other. Styrene-based polymers having the syndiotactic configuration of the present invention include polystyrene, poly(alkylstyrene), poly(halogenated styrene), poly(alkoxystyrene), poly(vinyl benzoate) and the mixtures thereof, and copolymers containing the above polymers as one of the components, having such a syndiotacticity that the proportion of racemic pentad is 30% or more, preferably 50% or more. The poly(alkylstyrene) can include poly(methylstyrene), poly(ethylstyrene), poly(isopropylstyrene), poly (tert-butylstyrene), poly(divinyl benzene), etc.; the poly(halogenated styrene) can include poly(chlorostyrene), poly (bromostyrene), poly(fluorostyrene), etc. Also, the poly(alkoxystyrene) can include poly(methoxystyrene), poly(ethoxystyrene), etc. Among these, particularly preferred styrene-based polymers include polystyrene, poly(p-methylstyrene), poly(m-methylstyrene), poly(p-tert-butylstyrene), poly(p-chlorostyrene), poly(m-chlorostyrene), poly(p-fluorostyrene), poly(divinyl benzene), and further a copolymer comprising at least one of the above polymers as partial component (Japanese Patent Application Laid-Open No. 187708/1987).

The molecular weight of the styrene-based polymer to be used in the present invention is not specifically limited, but the styrene-based polymer having a weight average molecular weight of 10,000 or more is preferred, and particularly that of 50,000 to 1,000,000 is optimum. If the weight average molecular weight is less than 10,000, mechanical properties are inferior and there is a tendency of lacking solvent resistance. Further, the molecular weight distribution thereof is also not limited, and the styrene-based polymer having various ranges can be used. Such a styrene-based polymer having syndiotactic configuration, has a melting point of 160 to 310°C and is extremely excellent in heat resistance, as compared with the conventional styrene-based polymer having atactic configuration.

Such a styrene-based polymer having syndiotactic configuration can be prepared by, for example, polymerizing a styrene-based monomer (a monomer corresponding to the above styrene-based polymer) using a titanium compound and a condensate product of water and trialkylaluminum as catalysts in an inert hydrocarbon solvent or in the absence of a solvent (see U.S. Patent No. 4,680,353).

On the other hand, the component (B) to be used in the present invention is represented by the following formula:



wherein R^1 and R^2 may be the same or different and each represent an alkyl group having 1 to 6 carbon atoms, an aryl group having 6 to 8 carbon atoms, a halogen atom or a hydrogen atom, and n is an integer of 50 to 500, preferably 100 to 450.

Specific examples of such polyphenylene ether resins include poly(2,6-dimethyl-1,4-phenylene)ether; poly(2,6-diethyl-1,4-phenylene)ether; poly(2-methyl-6-ethyl-1,4-phenylene)ether; poly(2-methyl-6-isopropyl-1,4-phenylene) ether; poly(2-methyl-1,4-phenylene)ether; poly(2,6-dichloro-1,4-phenylene)ether; poly(2-ethyl-6-bromo-1,4-phenylene)ether; poly(2-phenyl-1,4-phenylene)ether, etc. Among these, poly(2,6-dimethyl-1,4-phenylene)ether is particularly suitable. PPE to be used in the present invention is required to have an intrinsic viscosity in chloroform at 30°C of 0.28 dl/g or more, and preferably 0.3 to 0.66 dl/g. If the intrinsic viscosity is less than 0.28 dl/g, mechanical properties and solvent resistance become insufficient.

The composition of the present invention comprises the above component (A) and component (B) as main com-

ponents, and the blending ratio of both components is 10 to 98% by weight, preferably 20 to 95% by weight, more preferably 30 to 95% by weight of the component (A) and 90 to 2% by weight, preferably 80 to 5% by weight, more preferably 70 to 5% by weight of the component (B). If the component (A) is less than 10 % by weilght, solvent resistance is low and if it exceeds 98% by weight, elongation (toughness) is low. Also, if the component (B) exceeds 90% by weight, solvent resistance is low and thermal degradation of PPE becomes remarkable so that molding becomes difficult, and if it is less than 2% by weight, elongation is low.

The composition of the present invention further comprises a flame retarder as a component (C) and a flame-retardant aid as a component (D).

As the above flame retarder, various ones may be mentioned, but halogen-based flame retarders and phosphorus-based flame retarders are particularly preferred. The halogen-based flame retarders include, for example, tetrabromobisphenol A, tetrabromophthalic anhydride, hexabromobenzene, tribromophenylallyl ether, pentabromotoluene, pentabromophenol, tribromophenyl-2,3-dibromo propyl ether, tris(2,3-dibromopropyl)phosphate, tris(2-chloro-3-bromopropyl)phosphate, octabromodiphenyl ether, decabromodiphenyl ether, octabromobiphenyl, pentachloropentacyclodecane, hexabromocyclododecane, hexachlorobenzene, pentachlorotoluene, hexabromobiphenyl, decabromobiphenyl, decabromobiphenyl oxide, tetrabromobutane, decabromodiphenyl ether, hexabromodiphenyl ether, ethylene-bis-(tetrabromophthalimide), tetrachlorobisphenol A, tetrabromobisphenol A, oligomer of tetrachlorobisphenol A or tetrabromobisphenol A, halogenated polycarbonate oligomer such as brominated polycarbonate oligomer, halogenated epoxy compound, polychlorostyrene, brominated polystyrene such as poly(tribromostyrene), poly(dibromophenylene oxide), bis(tribromophenoxy)ethane, etc.

On the other hand, the phosphorus-based flame retarders include, for example, ammonium phosphate, tricresyl phosphate, triethyl phosphate, acidic phosphate, triphenylphosphene oxide, etc.

As the flame retarders among these, poly (tribromostyrene), poly(dibromophenylene oxide) and decabromodiphenyl ether are particularly preferred.

The above component (C) (flame retarder) is blended at a ratio of 3 to 40 parts by weight, preferably 5 to 35 parts by weight, more preferably 10 to 35 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount).

If the blending ratio of the component (C) is less than 3 parts by weight, flame retardance of the resulting composition is insufficient.

On the other hand, if it is added in excess of 40 parts by weight, flame retardance is not improved according to the ratio added, but rather the mechanical properties and solvent resistance are undesirably lowered.

As the flame-retardant aids, various ones may be mentioned, and they include, for example, antimony flame-retardant aids such as antimony trioxide, antimony pentoxide, sodium antimonate, metal antimony, antimony trichloride, antimony pentachloride, antimony trisulfide, antimony pentasulfide, etc. Also, in addition to the above, there may be mentioned zinc borate, barium metaborate, zirconium oxide, etc.

Among these, as the component (D), antimony trioxide is particularly preferred.

The component (D) (flame-retardant aid) is blended with a ratio of 1 to 15 parts by weight, preferably 2 to 10 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount).

If the blending ratio of the component (D) is less than 1 part by weight, the effects due to the flame-retardant aid are insufficient. On the other hand, if it exceeds 15 parts by weights, effects due to a flame-retardant aid are not improved according to the ratio added, but rather there exists the possibility of impairing other properties so that it is not preferred.

These components (C) and (D) are preferably blended in combination and when both components are used, a remarkably increased flame-retardant effect can be developed than in the case where only either one of the components (C) or (D) is used. Even small amounts of flame retarder and flame-retardant aid result in the increased flame-retardant effect since the component (B) is added.

Further, in the composition of the present invention, if necessary, a rubber-like elastomer and/or an inorganic filler may be blended as a component (E). These rubber-like elastomer and/or inorganic filler are blended in the above components (A) and (B) simultaneously with the above components (C) and (D), or separately from the components (C) and (D) so that mechanical properties, particularly impact resistance, etc. of the composition are further improved.

The rubber-like elastomer to be used as the component (E) may be various ones, but particularly suitable ones are a rubber-like copolymer containing a styrene-based compound as one component. There may be mentioned, for example, styrene-butadiene copolymer rubber (SBR), a rubber in which a part or all of the butadiene portion of a styrene-butadiene block copolymer is hydrogenated (SEBS), a styrene-isoprene copolymer rubber, a rubber in which a part or all of the isoprene portion of a styrene-isoprene block copolymer is hydrogenated, or as described in Japanese Patent Application No. 127100/1988, a granular elastomer obtained by polymerizing a vinyl-based monomer in the presence of the polymer obtained by polymerizing at least one monomer selected from the group consisting of an alkylacrylate, an alkylmetal methacrylate and a polyfunctional monomer having a conjugated diene type double bond, such as acrylonitrile-styrene grafted butadiene rubber (ABS), acrylonitrile-styrene grafted butadiene-butyl acrylate co-

polymer rubber (AABS), methyl methacrylate-styrene grafted butylacrylate rubber (MAS), styrene grafted butadiene rubber (SB), methyl methacrylate-styrene grafted butadiene rubber (MBS), methyl methacrylate-styrene grafted butadiene-butyl acrylate copolymer rubber (MABS), etc. Since these materials each have styrene structure, dispersibility in the above styrene-based polymer having syndiotactic configuration is good and as a result, improved effects in physical property is remarkable.

Further, examples of the rubber-like elastomer include, in addition to the above, natural rubber, polybutadiene, polyisoprene, polyisobutyrene, neoprene, ethylene-propylene copolymer rubber, polysulfide rubber, thiokol rubber, acrylic rubber, urethane rubber, silicone rubber, epichlorohydrin.

The above rubber-like elastomer is blended in the ratio of 5 to 85 parts by weight, preferably 10 to 50 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount). Mechanical properties, particularly impact resistance, are further improved by blending the rubber-like elastomer. If the blending ratio is less than 5% by weight, improvements in impact resistance or stretch are insufficient, while if it exceeds 85 parts by weight, improvement in heat resistance and solvent resistance are low.

As for the inorganic filler which can be used in place of the above rubber-like elastomer, or with the rubber-like elastomer as the component (E) in the present invention, it may be in the form of fiber, particles or powders. The fibrous inorganic filler includes glass fiber, carbon fiber, alumina fiber, etc., and glass fiber and carbon fiber are particularly preferred. As the shape of the glass fiber, there can be mentioned cross state, mat state, bundling cut state, short fiber, filament state, etc., but preferably the bundling cut state having a length of 0.05 mm to 13 mm and a diameter of the fiber of 5 to 20 μm, and particularly preferred are those which are treated with a silane series agent. Also, the carbon fibers preferably include polyacrylonitrile (PAN)-based ones, more preferably bundled materials of chopped fiber type having a length of 3 mm or so and a diameter of 7 to 15 μm.

On the other hand, as the particle and powder inorganic fillers, there can be mentioned talc, carbon black, graphite, titanium dioxide, silica, mica, calcium carbonate, calcium sulfate, barium carbonate, magnesium carbonate, magnesium sulfate, barium sulfate, oxysulfate, tin oxide, alumina, kaolin, silicon carbide, metal powder, etc., and talc, calcium carbonate and mica are particularly preferred. A preferred average particle size of talc is 0.3 to 20 μm, more preferably 0.6 to 10 μm. A preferred average particle size of calcium carbonate is 0.1 to 20 μm. A preferred average particle size of mica is 40 to 250 μm, more preferably 50 to 150 μm.

The above inorganic filler is blended in a ratio of 1 to 250 parts by weight, preferably 10 to 150 parts by weight based on 100 parts by weight of the above components (A) and (B) (total amount). If the blended ratio of the inorganic filler is less than 1 part by weight, sufficient effects due to the filler cannot be observed. On the other hand, if it exceeds 250 parts by weight, the filler cannot be dispersed uniformly and resulting composition becomes inferior in mechanical strength.

In the composition which comprises blending simultaneously the components (A) to (E), the component (C) is blended in a ratio of 3 to 40 parts by weight, preferably 5 to 35 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount).

The reason why the blending ratio is specified is the same as described in the explanation concerning the composition comprising the above components (A) to (D).

Regarding the component (D), it is blended in the ratio of 1 to 15 parts by weight, preferably 2 to 10 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount) as in the above. The reason why the blending ratio is specified is also as the same described in the explanation concerning the composition comprising the above components (A) to (D).

The composition of the present invention are prepared by blending the above components as defined in the claims. Various additives or other synthetic resins may further be blended, otherwise inhibiting the object of the present invention. As the aforesaid additive, there can be mentioned, for example, antioxidants such as phosphites and phosphates; UV absorbers such as benzotriazoles and benzophenones; external lubricants such as aliphatic carboxylates and paraffins; nuclear agents used conventionally, releasing agents, antistatic agents, coloring agents, etc. As the other synthetic resins, there can be mentioned resins such as polyethylene, polypropylene, polystyrene, AS resin, ABS resin, polymethylmethacrylate, etc.

The composition of the present invention can be obtained by blending the above components as defined in the claims and further various desired components, and then kneading at an optional temperature, for example, between a melting point and a temperature 80°C higher than the melting point. The blending and kneading procedures at this time can be carried out according to the conventional method. More specifically, the fusion-kneading method by using a kneader, a mixing roll, a uniaxial (monoaxial) or biaxial extruder, Banbury mixer, Henschel mixer or a kneading roll, or the solution blending method, etc. These compositions are molded into a tridimensional molding by the general method, preferably by an injection molding machine.

Also, in the molding and the process for producing the same of the present invention, a raw molding material is prepared by blending the above components (A) to (D), and further, if necessary, blending other components in optional amounts. The raw material is generally molded by an extrusion molding, a calendar molding, or further subjected to

injection molding in case of a blow molding or a blow stretch molding to form a preform for stretching (sheet, plate, film, tube, bottle, etc.). In this molding, the above raw material for molding is usually melted by heating and molded in the desired form by use of various molding machines, but the raw material for molding may be molded in a softened state without heat melting. The melting temperature of the raw material for molding is generally from its melting point to a temperature 80°C higher than its melting point. If the temperature is too high, undesirable problems occur, such as decomposition of the raw material for molding. Also, the thickness of the preform to be molded is not limited and is optionally selected, but generally it is usually chosen from the range of 5 mm or less, preferably 3 mm to 10 μm. If the thickness exceeds 5 mm, tension at stretching is large so that the stretching may sometimes become difficult. The crystallinity of the preliminary molding is 30% or lower, preferably 25% or lower.

In the process for producing the molding of the present invention, the above raw material for molding which has been heat melted is cooled at the time of molding for producing a preform having preferred crystallinity. Cooling should be carried out at a temperature lower than a temperature 30°C above, preferably 20°C above, the glass transition temperature of the composition. The cooling rate is 50 to 3°C/sec, preferably 50 to 5°C/sec.

In the process of the present invention, the preform thus obtained is heated to a temperature capable of effecting stretching. The temperature at this time should be set in the range between the glass transition temperature and the melting point of said composition.

Further, according to the process of the present invention, the preform heated to the temperature suitable for stretching is stretched uniaxially or biaxially. In the case of uniaxially stretching, the preform should be stretched at a draw ratio of at least 1.5-fold. If the draw ratio is less than 1.5-fold, strength and heat resistance become insufficient. Also, in the case of biaxially stretching, the preform should be stretched at a draw ratio of at least 1.2-fold to the respective stretching direction (biaxial direction). If the draw ratio is too small, strength and heat resistance of the resulting stretched molding become insufficient. In the above biaxially stretching, the preform may be stretched simultaneously in the machine direction (MD) and transverse direction (TD), or may be stretched sequentially in the desired order. As the means for stretching, there may be employed the means of tenter, milling, calendering, stretching between rolls, stretching due to gas pressure, etc.

In the process of the present invention, particularly in the case of biaxially stretching, the above raw material for molding can be directly subjected to inflation molding at the temperature of not more than its melting point without formation of a preform after heat melting to produce a biaxially stretched molding (e.g., a biaxially stretched film, etc.). In this inflation molding, it is effective so as to prevent melt fracture, roughness of surface and the like that the composition be maintained at a temperature of at least 20°C higher than its melting point. If, however, the melt temperature is too high, degradation of the composition becomes remarkable so that it is preferred to set the temperature within the range of the melting point to a temperature 80°C higher than the melting point. Further, the stretching temperature is preferably 5 to 150°C lower than the melting point and more preferably 10 to 50°C lower than the same. Also, if the blow-up ratio is decreased, uniaxially stretching is realized in inflation.

When the uniaxially stretching or biaxially stretching is carried out according to the process of the present invention, a stretched molding (sheet, plate, film, tube, bottle, etc.) having excellent heat resistance, solvent resistance and electric insulating properties can be obtained. Also, when dimensional stability at high temperature, and heat resistance is required, it is preferred to further carry out annealing. The annealing can be carried out by the conventional method, but the stretched molding is subjected to annealing under tension at a temperature ranging from 100°C, preferably a temperature higher than the glass transition temperature of said composition, to the melting point. By annealing at temperatures lower than glass transition temperature, thermal properties of the stretched molding cannot be improved, while at the temperature more than the melting point, the stretched molding is fused. The annealing is usually carried out for 0.5 seconds to 100 hours, preferably 0.5 seconds to 10 hours, further preferably 0.5 to 300 seconds. This annealing further increases heat resistance, dimensional stability, etc. of the stretched molding.

As described above, the styrene-based polymer composition comprising the styrene-based polymer and the polyphenylene ether resin of the present invention is remarkable excellent in solvent resistance. Further, the composition blended with the rubber-like elastomer is well balanced in mechanical properties, heat resistance, solvent resistance, etc.

Also, the resin composition of the present invention in which the flame retarder or the flame-retardant aid is further added, has sufficient flame retardance and also excellent mechanical properties, solvent resistance, etc.

Further, the stretched molding of the composition of the present invention has excellent mechanical strength and elongation while maintaining transparency, high modulus of elasticity and electric properties.

Accordingly, the composition of the present invention can be utilized for various fields including automobile parts such as exterior trim parts of an automobile, engine compartment parts, etc., as engineering plastics, and further for various machine parts, electric and electronic parts, domestic kitchenwares, etc. Also, the stretched molding of the present invention can be expected to be effectively used such as a film for electric field, e.g., a film for a flexible print substrate, an encapsulation film, etc., and a general film for industrial use such as magnetic tape, hot stamping, decoration and others.

The present invention is described in greater detail with reference to the following examples.

REFERENCE EXAMPLE 1 (Production of Polystyrene having Syndiotactic Configuration)

Two liters of toluene as a solvent, and 5 mmol of tetraethoxytitanium and 500 mmol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, and 15 L (L=liter) of styrene was added thereto at 55°C and polymerized for 4 hours.

After polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose the catalyst components, and then dried to obtain 2.5 kg of a styrene-based polymer (polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 97% by weight of an extraction residue. Said residue had a weight average molecular weight of 400,000, a number average molecular weight of 180,000, and a melting point of 269°C. A nuclear magnetic resonance analysis using carbon isotope (^{13}C-NMR Analysis, Solvent: 1,2-dichlorobenzene) of the polymer showed an absorption at 145.35 ppm, ascribable to the syndiotactic configuration. The syndiotacticity in terms of racemic pentad as calculated from the peak area was 98%.

REFERENCE EXAMPLE 2

Poly(2,6-dimethyl-1,4-phenylene)ether powder was obtained from GEM Polymer CO., Ltd. Intrinsic viscosity of this powder in chloroform at 30°C was 0.49 dl/g.

EXAMPLE 1

Zero point seven part by weight of (2,6-di-tert-butyl-4-methylphenylene)pentaerythritol diphosphite (Trade Name: PEP-36, produced by Adeka Argus Chemicals Co., Ltd.) and 0.1 part by weight of 2,6-di-tert-butyl-4-methylphenol (Trade Name: Sumilizer, produced by Sumitomo Chemical Co., Ltd.) were added to 100 parts by weight of a resin mixture consisting of 50% by weight SPS obtained in Reference Example 1 and 50% by weight poly(2,6-dimethyl-1,4-phenylene)ether described in Reference Example 2, and 12 parts by weight of polytribromostyrene and 3 parts by weight of antimony trioxide (Sb_2O_3) were mixed thereto further, and dry-blended. Then the blend was kneaded with the use of a twin screw kneading extruder, and pelletized.

The resulting pellet was made into three kinds of test pieces, that is, test pieces for tensile strength test, bending test, and flame retardance test in accordance with UL-94.

The result of flame retardance test using thus obtained test piece is shown in Table 4.

The results of dipping the bending test pieces in a regular gasoline similar to that of Example 1 are shown in Table 5. Moreover, elongation of tensile strength test piece were measured, respectively. The results are shown in Table 5.

EXAMPLES 2 to 9 and COMPARATIVE EXAMPLES 1 and 2

The procedure of Example 1 was repeated except that the substances shown in Table 1 were compounded in prescribed ratios as components (A) to (E), to obtain various test pieces, which were evaluated for physical properties in the same manner as in Example 1 . The results are shown in Tables 1 and 2.

REFERENCE EXAMPLE 3 (Production of Polystyrene having Syndiotactic Configuration)

Two liters of toluene as a solvent, and 1 mmol of cyclopentadienyltitanium trichloride and 0.8 mol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, and 3.6 L of styrene was added at 20°C and polymerized for 1 hour.

After the polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 330 g of a styrene-based polymer (polystyrene).

Said polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 95% by weight of an extraction residue. The polymer had a weight average molecular weight of 290,000, a number average molecular weight of 158,000 and a melting point of 270°C. A ^{13}C-NMR analysis showed an absorption at 145.35 ppm, ascribable to the syndiotactic configuration, and the syndiotacticity in terms of pentad as calculated from the peak area was 96%.

Table 1

No.	Component A		Component B		Component C		Component D	
	Styrene-based Polymer *1	wt%	Intrinsic viscosity of PPE resin *2	wt%	Flame retarder *3	part by weight *4	Flame-retardant aid	part by weight *4
Example 1	Syndiotactic	50	0.49	50	a	12	Sb_2O_3	3
Comparative Example 1	Syndiotactic	100	–	–	a	24	Sb_2O_3	6
Example 2	Syndiotactic	75	0.49	25	b	15	Sb_2O_3	5
Example 3	Syndiotactic	50	0.49	50	a	12	Sb_2O_3	3
Example 4	Syndiotactic	50	0.49	50	a	12	Sb_2O_3	3
Example 5	Syndiotactic	50	0.49	50	c	16	Sb_2O_3	4
Example 6	Syndiotactic	50	0.49	50	a	16	Sb_2O_3	4
Example 7	Syndiotactic	75	0.49	25	a	30	Sb_2O_3	8
Example 8	Syndiotactic	50	0.49	50	a	16	Sb_2O_3	4
Comparative Example 2	Atactic	50	0.49	50	a	12	Sb_2O_3	3
Example 9	Syndiotactic	90	0.49	10	a	24	Sb_2O_3	6

Table 1 (continued)

No.	Component E				Flame Retardance Test	
	Rubber-like elastomer *5	part by weight *4	Inorganic filler *5	part by weight *4	UL 94	Thickness (Inch)
Example 1	–	–	–	–	V-0	1/32
Comparative Example 1	–	–	–	–	V-0	1/32
Example 2	–	–	talc	15	V-0	1/32
Example 3	–	–	$CaCO_3$	15	V-0	1/32
Example 4	–	–	GF	43	V-0	1/32
Example 5	SB	15	–	–	V-0	1/32
Example 6	MAS	15	–	–	V-0	1/32
Example 7	MAS	40	GF	75	V-0	1/32
Example 8	SB	15	talc	15	V-0	1/32
Comparative Example 2	–	–	–	–	V-0	1/32
Example 9	–	–	GF mica	130 65	V-0	1/32

*1 Styrene-based polymer

Syndiotactic: Polystyrene having syndiotactic configuration, obtained in Reference Example 1

Atactic: Idemitsu Polystyrene US305, produced by Idemitsu Petrochemical Co., Ltd.

*2 PPE resin: Polyphenylene ether resin obtained in Reference Example 2

*3 Flame retarder

a: Polytribromostyrene ... Pyrocheck 68 PB, produced by Nissan Ferro Co.

b: Decabromodiphenyl ether ... Trade Name: SAYTEX 102, produced by Ethyl Corporation

C: Poly(dibromophenylene oxide) ... GLC PO-64P, produced by Great Lakes, Ltd.

*4 Proportion to the total amount of Component A and Component B as 100 parts by weight

*5 Rubber-like elastomer

SB: Styrene-grafted butadiene rubber (particle diameter: 0.7 μm, Name of Product on an trial basis: Metablen IP-2, produced by Mitsubishi Rayon Co., Ltd.)

MAS: Methyl methacrylate - n - butyl acrylate - styrene copolymer (Trade Name: KM 330, produced by Rohm & Haas Company)

*6 Inorganic filler

GF: Glass fiber (Length of fiber: 3 mm, Diameter: 13 μm, CS03 MA 429A, produced by Asahi Fiber Glass Co., Ltd.)

talc: (Average particle diameter: 0.6 μm, Talc FFR, produced by Asada Seifun Co.)

$CaCO_3$: Calcium carbonate having average particle diameter of 2 μm

Table 2

No.	Tensile Fracture elongation (%)	Bending strength (kg/cm)	Gasoline- *1 Dipping Test
Example 1	4	1470	A
Comparative Example 1	1	980	A
Example 2	4	1260	A
Example 3	5	1250	A
Example 4	5	1600	A
Example 5	20	1060	A
Example 6	18	1070	A
Example 7	16	1520	A
Example 8	16	1070	A
Comparative Example 2	3	1290	C
Example 9	-	1730	A

*1 Left for one week at room temperature
A ... No change in appearance
B ... Swollen (not less than 10% of increase in weight)
C ... Dissolved

Claims

1. A styrene-based polymer composition which comprises

(A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more and
(B) 90 to 2% by weight of PPE having an intrinsic viscosity of 0.28 dl/g or more at 30°C in chloroform, and
(C) 3 to 40 parts by weight of a flame retarder and
(D) 1 to 15 parts by weight of a flame-retardant aid based on 100 parts by weight of the total amount of (A) and (B).

2. A styrene-based polymer composition which comprises

(A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more and
(B) 90 to 2% by weight of a polyphenylene ether having an intrinsic viscosity of 0.28 dl/g or more at 30°C in chloroform, and
(E) 5 to 85 parts by weight of a rubber-like elastomer or 1 to 250 parts by weight of an inorganic filler based

on 100 parts by weight of the total amount of (A) and (B).

3. A styrene-based polymer composition which comprises

(A) 10 to 98% by weight of a styrene-based having syndiotactic configuration with a racemic pentad of 30% or more and
(B) 90 to 2% by weight of PPE having an intrinsic viscosity of 0.28 dl/g or more at 30°C in chloroform, and
(C) 3 to 40 parts by weight of a flame retarder,
(D) 1 to 15 parts by weight of a flame-retardant aid and
(E) 5 to 85 parts by weight of a rubber-like elastomer or 1 to 250 parts by weight of an inorganic filler based on 100 parts by weight of the total amount of (A) and (B).

4. A styrene-based polymer composition according to Claims 1 or 3, wherein the flame retarder of said component (C) is at least one compound selected from decabromodiphenyl ether, polytribromostyrene and poly(dibromophenylene oxide).

5. A styrene-based polymer composition according to any one of Claims 1, 3 or 4, wherein the flame-retardant aid of said component (D) is antimony trioxide.

6. A styrene-based polymer composition according to of Claims 2 or 3, wherein the rubber-like elastomer of said component (E) is a rubber-like elastomer containing a styrene-based compound as a partial component thereof.

7. A styrene-based polymer composition according to Claims 2 or 3, wherein the inorganic filler of said component (E) is glass fiber.

Patentansprüche

1. Polymerzusammensetzung auf der Basis von Styrol, die umfaßt:

(A) 10 bis 98 Gew.-% eines Polymers auf der Basis von Styrol, das eine syndiotaktische Konfiguration mit 30 % oder mehr racemischen Pentaden aufweist, und (B) 90 bis 2 Gew.-% PPE mit einer intrinsischen Viskosität von 0,28 dl/g oder mehr bei 30°C in Chloroform, und
(C) 3 bis 40 Gewichtsteile eines Flammschutzmittels und
(D) 1 bis 15 Gewichtsteile eines Flammschutzhilfsstoffs, bezogen auf 100 Gewichtsteile der Gesamtmenge von (A) und (B).

2. Polymerzusammensetzung auf der Basis von Styrol, die umfaßt:

(A) 10 bis 98 Gew.-% eines Polymers auf der Basis von Styrol, das eine syndiotaktische Konfiguration mit 30 % oder mehr racemischen Pentaden aufweist, und (B) 90 bis 2 Gew.-% PPE mit einer intrinsischen Viskosität von 0,28 dl/g oder mehr bei 30°C in Chloroform, und
(E) 5 bis 85 Gewichtsteile eines kautschukartigen Elastomers oder 1 bis 250 Gewichtsteile eines anorganischen Füllstoffes, bezogen auf 100 Gewichtsteile der Gesamtmenge von (A) und (B).

3. Polymerzusammensetzung auf der Basis von Styrol, die umfaßt:

(A) 10 bis 98 Gew.-% eines Polymers auf der Basis von Styrol, das eine syndiotaktische Konfiguration mit 30 % oder mehr racemischen Pentaden aufweist, und
(B) 90 bis 2 Gew.-% PPE mit einer intrinsischen Viskosität von 0,28 dl/g oder mehr bei 30°C in Chloroform, und
(C) 3 bis 40 Gewichtsteile eines Flammschutzmittels und
(D) 1 bis 15 Gewichtsteile eines Flammschutz-Hilfsstoffs,
(E) 5 bis 85 Gewichtsteile eines kautschukartigen Elastomers oder 1 bis 250 Gewichtsteile eines anorganischen Füllstoffes, bezogen auf 100 Gewichtsteile der Gesamtmenge von (A) und (B).

4. Polymerzusammensetzung auf der Basis von Styrol nach Anspruch 1 oder 3, worin das Flammschutzmittel der erwähnten Komponente (C) mindestens eine Verbindung ist, die ausgewählt wird aus Decabromdiphenylether, Polytribromstyrol und Poly(dibromphenylenoxid).

5. Polymerzusammensetzung auf der Basis von Styrol nach irgendeinem der Ansprüche 1, 3 oder 4, worin der Flammschutz-Hilfsstoff der erwähnten Komponente (D) Antimontrioxid ist.

6. Polymerzusammensetzung auf der Basis von Styrol nach irgendeinem der Ansprüche 2 oder 3, worin das kautschukartige Elastomer der erwähnten Komponente (E) ein kautschukartiges Elastomer ist, das eine Verbindung auf der Basis von Styrol als partielle Komponente davon enthält.

7. Polymerzusammensetzung auf der Basis von Styrol nach Anspruch 2 oder 3, worin der anorganische Füllstoff der erwähnten Komponente (E) eine Glasfaser ist.

Revendications

1. Composition de polymère à base de styrène qui comprend

   (A) 10 à 98% en poids d'un polymère à base de styrène ayant une configuration syndiotactique avec une proportion de racémique pentavalent de 30% ou plus, et
   (B) 90 à 2% en poids de PPE ayant une viscosité intrinsèque de 0,28 dl/g ou plus à 30°C dans le chloroforme, et
   (C) 3 à 40 parties en poids d'un retardateur de flamme, et
   (D) 1 à 15 parties en poids d'un additif retardateur de flamme par rapport à 100 parties en poids de la quantité totale de (A) et de (B).

2. Composition de polymère à base de styrène qui comprend

   (A) 10 à 98% en poids d'un polymère à base de styrène ayant une configuration syndiotactique avec une proportion de racémique pentavalent de 30% ou plus, et
   (B) 90 à 2% en poids de PPE ayant une viscosité intrinsèque de 0,28 dl/g ou plus à 30°C dans le chloroforme, et
   (E) 5 à 85 parties en poids d'un élastomère caoutchouteux ou 1 à 250 parties en poids d'une charge minérale par rapport à 100 parties en poids de la quantité totale de (A) et(B).

3. Composition de polymère à base de styrène qui comprend

   (A) 10 à 98% en poids d'un polymère à base de styrène ayant une configuration syndiotactique avec une proportion de racémique pentavalent de 30% ou plus, et
   (B) 90 à 2% en poids de PPE ayant une viscosité intrinsèque de 0,28 dl/g ou plus à 30°C dans le chloroforme, et
   (C) 3 à 40 parties en poids d'un retardateur de flamme,
   (D) 1 à 15 parties en poids d'un additif retardateur de flamme, et
   (E) 5 à 85 parties en poids d'un élastomère caoutchouteux ou 1 à 250 parties en poids d'une charge minérale par rapport à 100 parties en poids de la quantité totale de (A) et (B).

4. Composition de polymère à base de styrène selon les revendications 1 ou 3, où le retardateur de flamme dudit composant (C) est au moins un composé choisi parmi les éther de décabromodiphényle, polytribromostyrène et poly(oxyde de dibromophénylène).

5. Composition de polymère à base de styrène selon l'une quelconque des revendications 1, 3 ou 4, où l'additif retardateur de flamme dudit composant (B) est le trioxyde d'antimoine.

6. Composition de polymère à base de styrène selon l'une quelconque des revendications 2 ou 3, où l'élastomère caoutchouteux dudit composant (E) est un élastomère caoutchouteux contenant un composé à base de styrène en tant que composant partiel.

7. Composition de polymère à base de styrène selon les revendications 2 ou 3, où la charge minérale dudit composant (E) est de la fibre de verre.